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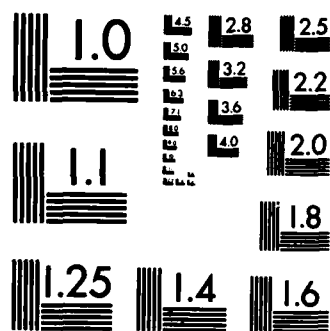
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(U) PENTAFLUOROSULFUR COMPOUNDS FOR NAVAL MATERIALS
UNIVERSITY OF TEXAS
AUSTIN, TX 78712
COWLEY, A H

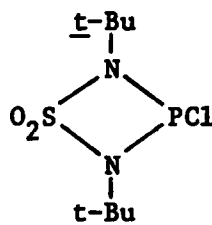
FINAL REPORT

Contract N00014-76-C-0577

In the interest of organizational simplicity, this final report is discussed under three separate headings.

(1) Cyclic Sulfur-Nitrogen Compounds

The sulfamide, $(t\text{-BuNH})_2\text{SO}_2$, turned out to be a rich source of novel sulfur-nitrogen heterocycles. For example, treatment of $(t\text{-BuNH})_2\text{SO}_2$ with PCl_3 in the presence of a base such as Et_3N produced the first S-N-P(III) ring compound, 1.



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In turn, compound 1 proved to be a very valuable intermediate for the synthesis of numerous other cyclic derivatives as shown in the scheme below:

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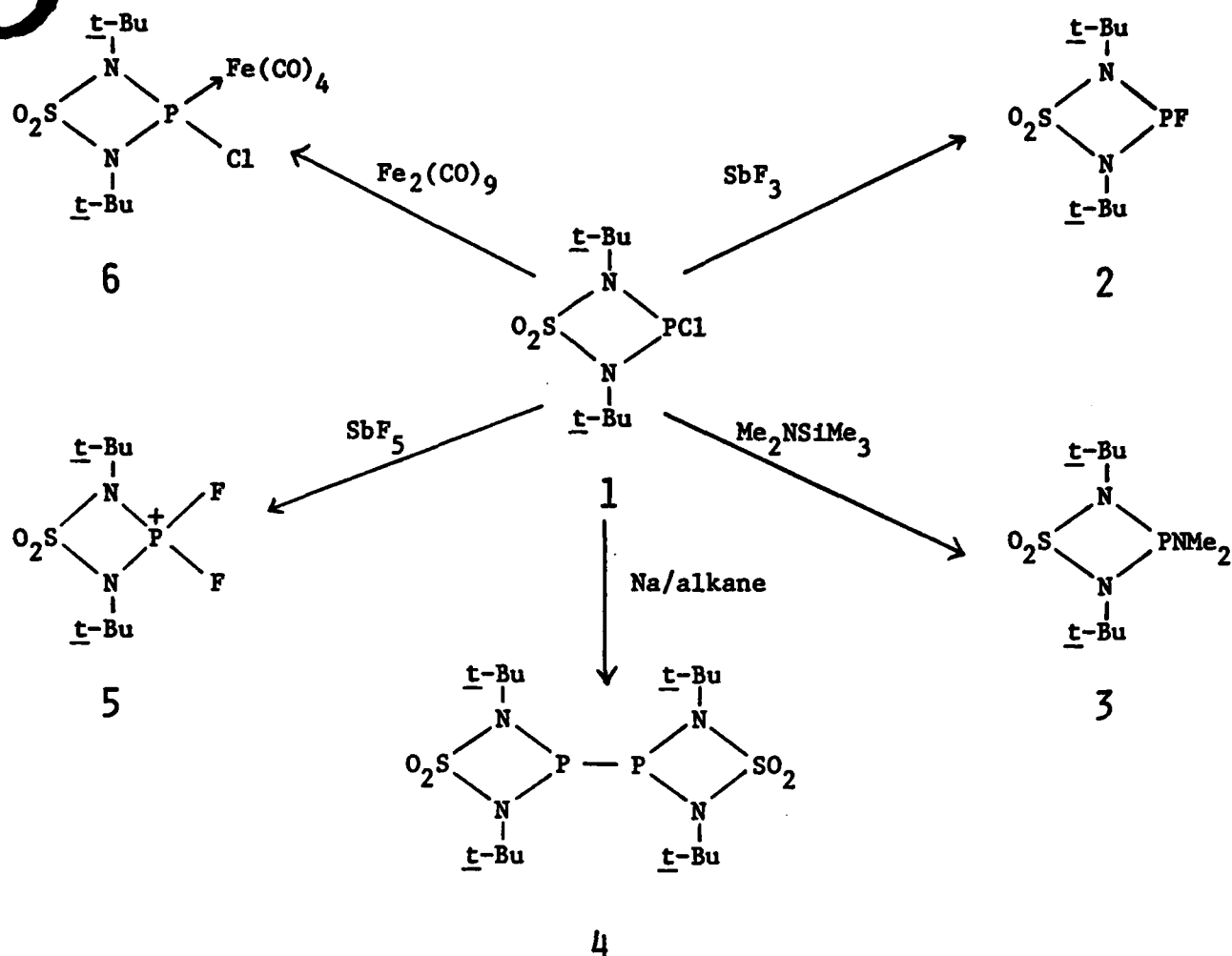
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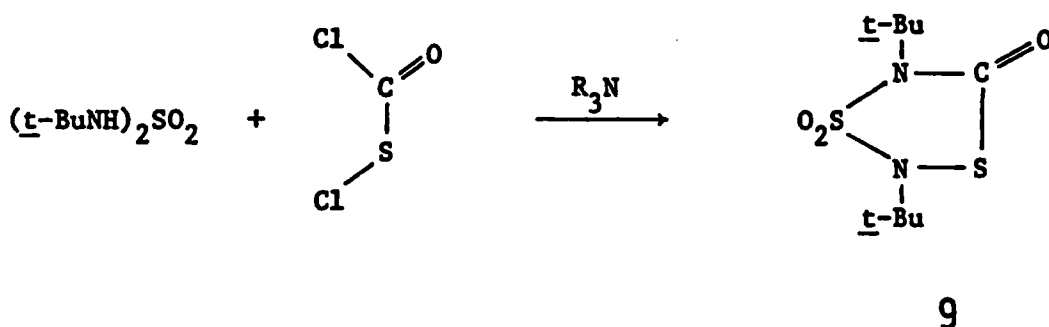
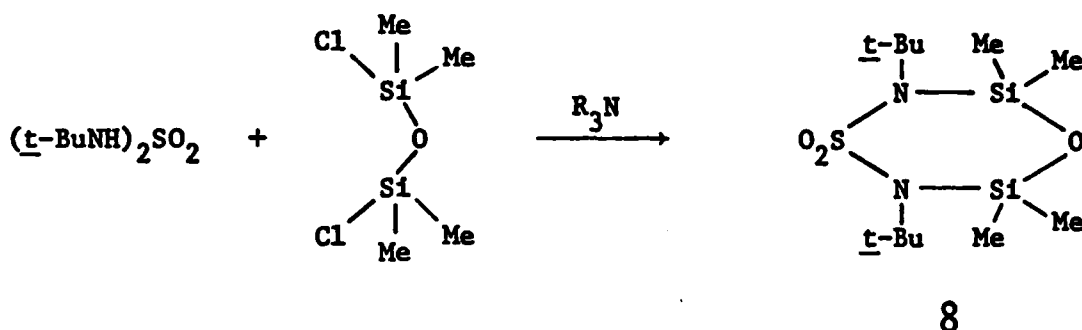
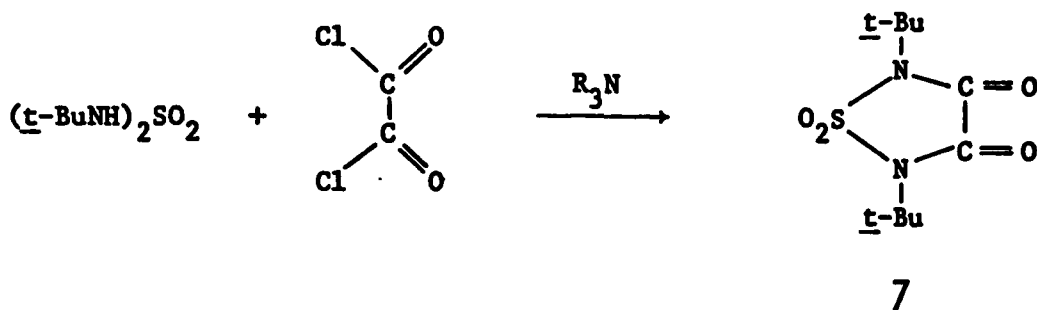
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Of these reactions, the one leading to compound 5 is particularly interesting because it involves the net transfer of F^+ to a P-F bond. Presumably compound 5 is produced via a two-step process involving oxidative fluorination of 1 to a trifluorophosphorane followed by F^- abstraction.

Several other novel heterocycles have been produced² by the action of $(\text{t-BuNH})_2\text{SO}_2$ on active halides in the presence of a tertiary amine as shown below:



Of the above compounds, 9 is particularly significant because it represents a rare example of a ring system involving sulfur in two different oxidation states.

In view of the synthetic importance of $(\text{t-BuNH})_2\text{SO}_2$, an X-ray crystal structure of this compound was undertaken. Our study³ is the first X-ray structure work on a dialkylsulfamide. Significant features of the structure (Figure 1) are (a) the nitrogen geometry of both t-BuNH groups is between trigonal planar and tetrahedral, and (b) the sulfamide adopts an $\text{anti}(\text{C}_2)$ conformation rather than the $\text{cis}(\text{C}_s)$ conformation presumably due to minimization of steric interactions between the t-butyl groups.

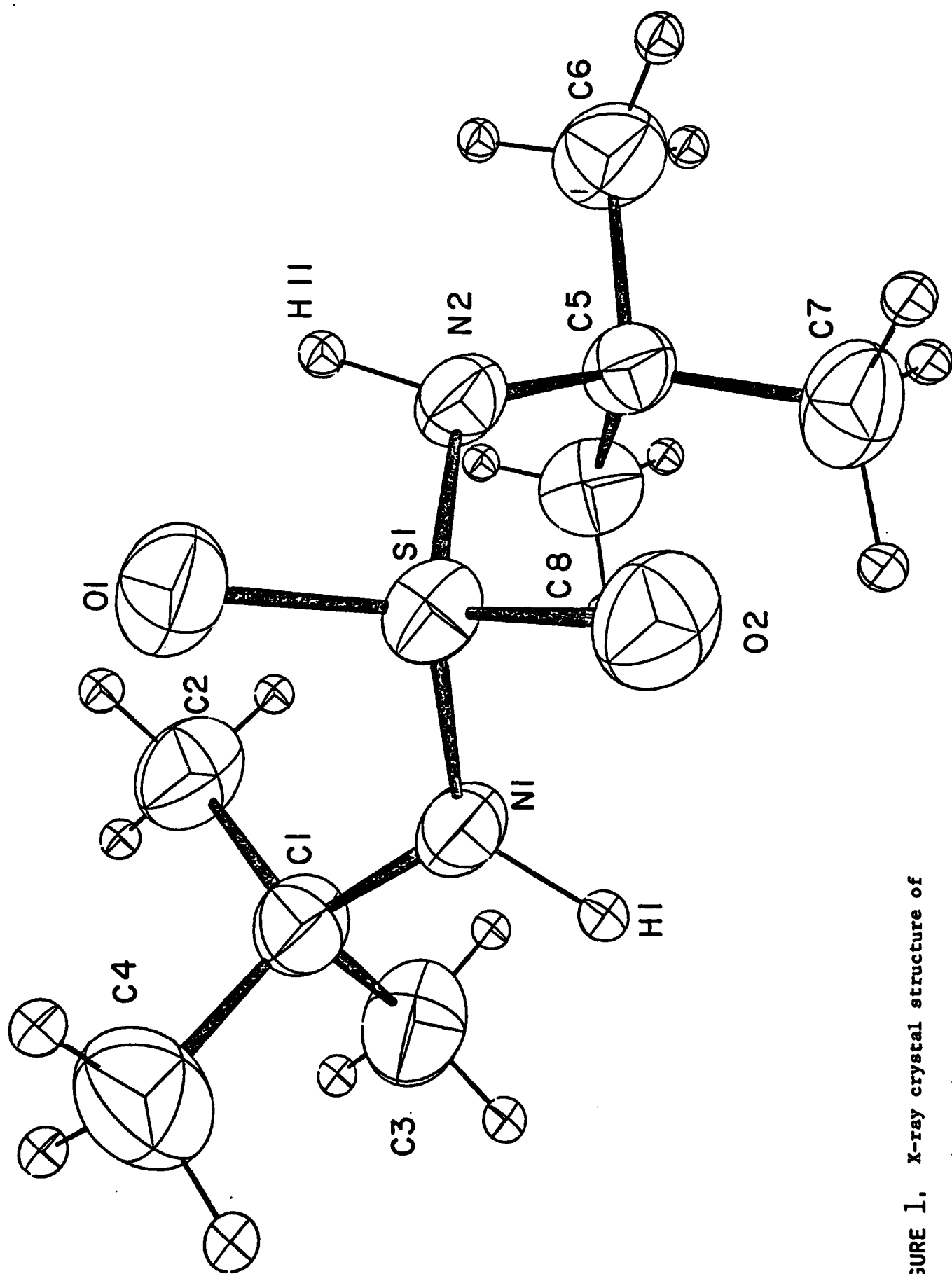
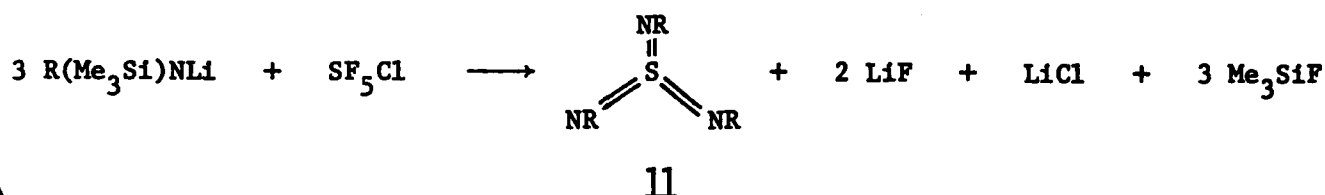
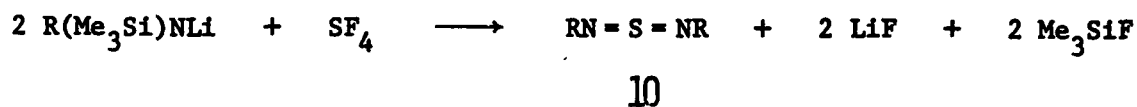


FIGURE 1. X-ray crystal structure of $(t\text{-BuNH})_2\text{SO}_2$.

↓
(b) Bulky Ligand Chemistry of Sulfur

The reaction of bulky amides, $R(\text{Me}_3\text{Si})\text{NLi}$, with S-F or S-Cl bonds with concomitant elimination of Me_3SiF has provided an excellent route to compounds of types **10** and **11** which feature S=N bonds as shown below:

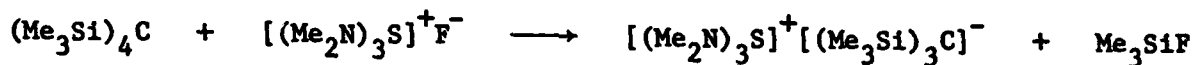
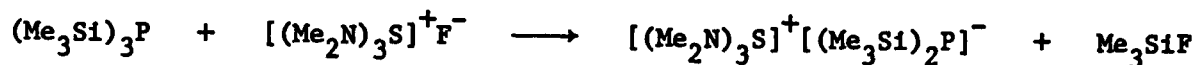


↙ Current efforts are concerned with the introduction of bulky carbon ligands on to sulfur with a view to producing novel compounds with sulfur-carbon double bonds. One of the ligands which is used for this purpose is $(\text{Me}_3\text{Si})_2\text{CH}$. The most common way of introducing this particular ligand is via the action of $n\text{-BuLi}$ on $(\text{Me}_3\text{Si})_2\text{CHCl}$. Previous preparations of this intermediate have involved several steps and a low overall yield. We have now developed a convenient "one-pot" synthesis of $(\text{Me}_3\text{Si})_2\text{CHCl}$.⁴

→ (c) Sulfur-Nitrogen Cations

In an earlier progress report,⁵ we noted that SF_4 reacts readily with tris-(dialkylamino)boranes, $(\text{R}_2\text{N})_3\text{B}$, to afford tris(dialkylamino)sulfonium cations, $[(\text{R}_2\text{N})_3\text{S}]^+$, as their $[\text{BF}_4]^-$ salts. By means of anion exchange reactions, it is possible to produce good yields of the corresponding fluorides, $[(\text{R}_2\text{N})_3\text{S}]\text{F}$. Tris(dialkylamino)sulfonium fluorides are proving to be important reagents for producing synthetically useful anions in a highly reactive form. The synthetic strategy depends on the very high affinity of silicon for fluorine due to the

large bond enthalpy of the Si-F bond (135 kcal/mol). The following equations illustrate how we have been able to produce high yields of silylated phosphide anions and carbanions.⁶



This approach should have wide applicability for both organic and inorganic synthesis.

The persulfurane, SF_5Cl , has been treated with $(\text{Me}_2\text{N})_3\text{B}$ and $(\text{Et}_2\text{N})_3\text{B}$ in an effort to prepare persulfonium cations, $[(\text{R}_2\text{N})_5\text{S}]^+$, which would be isoelectronic with the corresponding pentakis(amido)phosphoranes. However, we have found⁷ that the cationic products of these reactions are, in fact, tris(dialkylamino)-sulfonium ions, $[(\text{R}_2\text{N})_3\text{S}]^+$, as a consequence of the reduction of S(VI) to S(IV), i.e.



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- (4) A. H. Cowley and R. A. Kemp, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 11, 591 (1981), (TR 81-01).
- (5) A. H. Cowley, D. J. Pagel, and M. L. Walker, Journal of the American Chemical Society, 100, 7065 (1978), (TR 78-01).
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- TR 78-02 A. H. Cowley, M. Lattman, and M. Walker, Journal of the American Chemical Society, 101, 5224 (1979).
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- TR 81-02 J. L. Atwood, A. H. Cowley, W. E. Hunter, and S. K. Mehrotra, Inorganic Chemistry, 21, 435 (1982).

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